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(54) Perfume and bleach compositions

Parfüm und Bleichmittel enthaltende Zusammensetzungen

Compositions contenant un parfum et des agents de blanchiment

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(56) References cited:
EP-A- 0 005 618 EP-A- 0 147 191
EP-A- 0 214 789 JP-A-60 245 699
US-A- 4 289 641

• **DERWENT JAPANESE PATENTS REPORT, vol.**
86, no. 04, Section Ch. D, page 13; & JP-A-60
245 699

• **Parfümerie und Kosmetik, vol. 61, no. 8, 1980,**
pages 285-289; B. Streschnak: "Probleme bei
der Parfümierung von Waschpulvern"

Remarks:

The file contains technical information submitted
after the application was filed and not included in
this specification

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Description**FIELD OF THE INVENTION:**

5 The invention relates to perfume compositions which are stable to a commercially usable level in the presence of bleaching compositions comprising organic peracid bleaching materials. The invention also relates to bleaching compositions containing such perfumes. These bleaching compositions are particularly, but not exclusively, suited to the bleaching of fabrics, and for this purpose they may also contain detergent active compounds.

BACKGROUND TO THE INVENTION :

There has long existed a problem in the formulation of bleaching compositions in that the effective perfuming of such compositions is difficult to achieve. The perfume is required to remain stable at a commercially usable level during storage prior to use and then be available for effective delivery to the surface without being altered or destroyed by the bleach component.

Perfume is added to a bleach composition, in particular a detergent composition, to provide an olfactory benefit in the product during use and to enhance the olfactory properties of the treated surface.

The effective perfuming of fabric, as an example of surfaces, that has already been bleached and washed can be achieved by incorporation of a suitable perfume in a fabric conditioner to be added during the rinsing or drying stage subsequent to a bleaching and washing step, but this necessitates the introduction of an additional step in the laundry process.

The use of peracids in detergent formulations presents a particularly hostile environment for perfume compositions. The present invention provides organic peracid bleach-stable perfume compositions. It is also known to generate a peracid bleaching species in the wash liquor by incorporating a peroxide bleach material, for example sodium perborate, and a bleach precursor, for example N, N,N¹, N¹-tetraacetyl ethylene diamine (TAED). The present invention does not relate to these systems in which the peracid bleach species is formed in situ.

US-A-4289641 discloses deodorant detergent products comprising a soap, detergent adjuncts including a detergency builder (other than soap) and/or a bleach such as an organic peroxyacid, and a deodorant composition. The deodorant composition comprises a special combination of a plurality of deodorant active components selected from several different defined classes.

JP-A-60 245699 discloses a bleaching detergent composition comprising at least one perfume agent, monopersulphate bleach, zeolite and surfactant.

EP-A-0214789 discloses a dry, diperacid-based bleach product, which may comprise a fragrance component stabilised by isolation from the bleaching composition.

EP-A-0147191 discloses a bleach-stable deodorant perfume comprising perfume components which are judged to be stable in the presence of sodium perborate tetrahydrate and TAED bleach activator.

EP-A-0005618 discloses deodorant products other than for use on human skin, comprising a deodorant composition and a carrier therefor chosen from abrasive cleaners, bleaching agents, waxes, film-forming polymers or mixtures thereof. The deodorant composition comprises a special combination of a plurality of deodorant active components selected from several different defined classes, as in US-A-4289641 mentioned above.

GENERAL DESCRIPTION OF THE INVENTION:

In its widest aspect, the invention provides a bleach composition comprising an organic peracid bleach and a perfume composition comprising perfume components which do not contain alkenyl or alkynyl groups and have a PSV (as defined hereafter) of at least 65%, selected from the following classes:

- i) saturated alcohols
- ii) saturated esters
- iii) saturated aromatic ketones
- iv) saturated lactones
- v) saturated nitriles
- vi) saturated ethers
- vii) saturated acetals
- viii) saturated phenols
- ix) saturated hydrocarbons, and
- x) saturated aromatic nitromusks

the said perfume components constituting from 0.05 to 1% by weight of the bleach composition.

The terms "saturated" is used herein to define groups not containing alkenyl or alkynyl bonds.

In a more specific aspect, the invention provides a bleach composition as defined above comprising an effective amount of the organic peracid bleach and up to 10% by weight of the defined peracid-stable perfume composition.

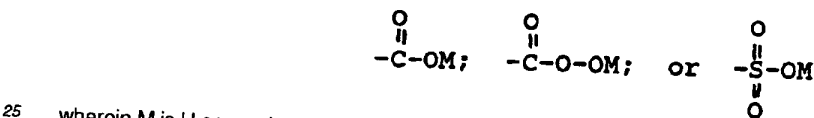
5 Preferably, the peracid-stable perfume compositions for use in the present invention will contain at least 80%, preferably 90% by weight, of the components defined above. Preferably, the components listed will have PSV's of at least 80%.

The bleach composition may also contain detergent active materials and will be referred to as bleach and/or detergent composition in the further description of this invention. The term organic peracid bleach, as used herein, includes the organic peroxyacids and their salts, which are well described in the literature as having the ability of effective bleaching at lower wash temperatures of about 20°-60°C.

The organic peroxy acids usable in the present invention are compounds having the general formula :

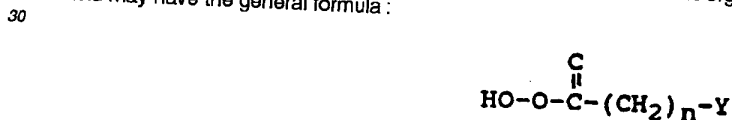


wherein R is an alkylene or substituted alkylene group containing 1 to 20 carbon atoms or an arylene group containing from 6 to 8 carbon atoms, n is 0 or 1, and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous solution. Such Y groups can include, for example :



25 wherein M is H or a water-soluble, salt-forming cation. Where n = 0, they are sometimes also referred to as peroxycarboxylic acids and where n = 1, they belong to the class of per(oxy)carbonic acids.

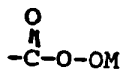
Preferred organic peroxyacids are solid at room temperature up to about 40°C. They can contain either one, two or more peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted acid may have the general formula :



wherein Y can be H, -CH₃, -CH₂Cl,



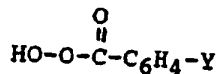
40 or



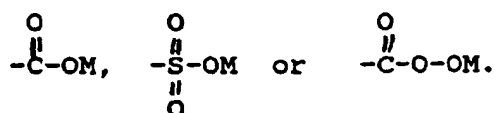
45 and n can be an integer from 1 to 20, preferably from 4-16.

Examples of peroxyacids are peroxydodecanoic acids, peroxytetradecanoic acids and peroxyhexadecanoic acids, particularly 1,12-diperoxydodecanedioic acid being preferred. Other examples of suitable aliphatic peroxyacids are diperoxyazelaic acid, diperoxyadipic acid, diperoxysebacic acid and alkyl(C₁-C₂₀) dipersuccinic acids.

50 When the organic peroxyacid is aromatic, the unsubstituted acid may have the general formula :



55 wherein Y is, for example, hydrogen, halogen, alkyl,



The percarboxy and Y groupings can be in any relative position around the aromatic ring. The ring and/or Y group (if alkyl) can contain any non-interfering substituents such as halogen or sulphonate groups. Examples of suitable aromatic peroxyacids and salts thereof include monoperoxyphthalic acid; diperoxyterephthalic acid; 4-chlorodiperoxyphthalic acid; diperoxyisophthalic acid; peroxy benzoic acids and ring-substituted peroxy benzoic acids, such as m-chloroperbenzoic acid and peroxy-alpha-naphthoic acid; and also magnesium monoperphthalate (obtainable under the tradename "H48" from Interlox Chemicals Ltd).

Further examples of organic peroxyacid bleach compounds are described in the following patent literature : EP-A-0083560; EP-A-0105689; EP-A-0083560; EP-A-0166571; EP-A-0168204; EP-A-0195570; EP-A-0206624; and EP-A-0170386.

All these peracid compounds are usable in the bleach and/or detergent compositions of the invention and may be present in an amount of from 0.5 to 65% by weight of the total composition, preferably from 1-50%, particularly preferably from 1-25% by weight.

At these levels, the peracid bleach will be effective to give in the following test an increase in stain removal from tea-stained cotton of at least two reflectance units more than a similar product in which the peracid is replaced by sodium sulphate.

The tea-stained cotton is prepared as follows. A length of cotton sheeting is boiled for 1 hour in a concentrated infusion of tea. The cloth is removed, rinsed thoroughly, and dried at room temperature. The peracid is tested in the following product:

Component (on anhydrous basis)	Parts by Weight
Linear alkyl (C12 to C18) benzene sulphonate	9
Nonionic 7EO	4
Sodium tripolyphosphate	33
Sodium alkaline silicate	6
Sodium carboxymethylcellulose	1
Magnesium silicate	1
Ethylene diaminetetraacetic acid	0.2
Water	10.8
Sodium sulphate	see below

The level of sodium sulphate is adjusted so that, after addition of the bleach, the parts by weight of the total formulation add up to 100.

4 gms of product is dissolved in 1 litre of 0°H water, and the pH of the solution is adjusted to equal the pKa of the peracid under test, using small quantities of sulphuric acid or sodium hydroxide solution. The test cloths are washed at 40°C for 30 mins in a Tergotometer operating at 75 r.p.m. After the wash the test cloths are rinsed and dried. The reflectances of the cloths at 460 nm are read before and after washing, using an Elrepho reflectometer fitted with an external filter to cut out incident radiation of less than about 400 nm. (Elrepho is a Trade Mark).

It is to be noted this test method defines the peracid environment in which the perfume compositions of the invention are usable. The increase of at least two reflectance units in the bleach activity will be dependent on the type of peracid used and its level in the formulation.

The peracid stability values, abbreviated herein to PSV, of perfume components were established by storage in a laundry powder base containing a peracid component.

A laundry powder base with the formulation quoted was prepared.

<u>Component</u>	<u>Parts by wt</u>
Linear alkyl (C12-C18) benzen sulphonate	9.0
Nonionic surfactant (Synperonic [®] A7)	4.0
Sodium tripolyphosphate	33.0
Alkaline sodium silicate	6.0
Trade mark	
Sodium carboxymethylcellulose	1.0
Magnesium silicate	1.0
EDTA	0.2
Sodium sulphate	15.0
Water	10.8
Peracid granules	20.0

	100.0

The peracid granules were obtained from Degussa GmbH of West Germany and had the composition :

Component	% wt
Alpha, omega-Diperoxydodecanedioic acid (DPDDA)	12.0
Magnesium sulphate	4.0
Sodium sulphate	83.0
Binder	1.0
	<u>100.0</u>

Laundry powder base (500 g) was dosed with perfume material (1.5 g) and then passed through a 20 mesh sieve. The remainder of the base powder (300 g) was added to the sieved base, placed in a Y-cone blender and blended for 10 minutes. After 10 minutes, DPDDA granules (200 g, 12% DPDDA content) were added and the whole was blended for a further 20 minutes.

Samples were taken from each port of the Y-cone blender and combined (10 g total) for initial analysis. The remainder was sampled into two sealed glass jars. The jar samples were stored at 0°C (control sample) and 37°C for 4 weeks. After storage, the perfume was extracted from the samples (solvent extraction with a suitable solvent) and analysed by gas-chromatography (gc), to determine the percentage of each perfume ingredient remaining relative to the control.

The analytical procedure was repeated ten times for a range of five perfume materials. Statistical analysis of the gc data gave an average percentage coefficient of variance of 1.25.

Results

The test method described was applied to a number of perfume components and the peracid stability values (PSV) quoted as a percentage in Table I.

Table IPSV (%)

5	i) Saturated alcohols:	
	Tetrahydrogeraniol	81
	Decanol	100
10	Phenylethyl alcohol	92
	Phenylpropyl alcohol	100
	o-tert-Butylcyclohexanol	100
15		
	Dihydroterpineol	90
	di-Isobutylcarbinol	100
20	2,6-Dimethyl-2-heptanol	89
	Tetrahydrolinalol	88
25	ii) Saturated esters:	<u>PSV (%)</u>
	Tetrahydrolinalyl acetate	86
	MenthyI acetate	88
30	ortho-tert-Butylcyclohexyl acetate	100
	Dimethyl benzyl carbinyI acetate	99

35

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	iii) Saturated aromatic ketones:	<u>PSV (%)</u>
5	Tonalid (6-acetyl-1,1,3,4,4,6-hexamethyltetrahydronaphthalene obtainable from PFW of Amersfoort, Netherlands)	74
10	Benzophenone	98
	Methyl naphthyl ketone	76
15	Traseolide (6-acetyl-1-isopropyl-2,3,3,5-tetramethylindane from Quest International of the Netherlands)	58
20	Celestolide (4-acetyl-6-tertbutyl-1,1-dimethyl indane from IFF of Union Beach, NJ, USA)	83
	iv) Saturated lactones:	<u>PSV (%)</u>
25	Hexadecanolide	92
	Sclareolide	73
30	Lactoscatone (gamma-lactone of 1-hydroxy-3,10,10-trimethyl-bicyclo [4,4,10] decane-3-carboxylic acid and isomers from Dragoco of Holzminden, Germany)	82
	v) Saturated nitriles:	<u>PSV (%)</u>
40	Frutonile (2-methyldecanonitrile from Quest International of Ashford, England)	98
	Dodecyl nitrile	100
45	Frescile (3-methyldodecanonitrile from Quest International)	100
	vi) Saturated ethers:	<u>PSV (%)</u>
50	Cedramber (cedryl methyl ether from IFF)	81
55	Anther (Iso-amyl phenylethyl ether	

	from Quest International)	100
	Ph nylethyl methyl ether	93
5		
	vii) Saturated acetals:	<u>PSV (%)</u>
	Herboxane (2-butyl-4,4,6-trimethyl	
10	dioxan from Quest International)	69
	Indolal (indano [1,2-d]1,3-dioxane from	
	Dragoco)	100
15		
	viii) Saturated phenols:	<u>PSV (%)</u>
	Carvacrol	84
20		
	ix) Saturated hydrocarbons:	<u>PSV (%)</u>
	Diphenyl methane	99
	para-Cymene	99
25		
	x) Saturated aromatic nitromusks:	<u>PSV (%)</u>
	Moskene (Musk cymene from Givaudan	
30	of Geneva, Switzerland)	96
	xi) Saturated salicylates:	<u>PSV (%)</u>
	Hexyl salicylate	51
35	Amyl salicylate	34
	Isoamyl salicylate	10
	Benzyl salicylate	0
40		
	xii) Saturated aldehydes:	<u>PSV (%)</u>
	Dodecanal	0
45	Lilial (3- / para-tert.butylphenyl)	
	-2-methylpropanal from Givaudan)	0
50	xiii) Saturated formates:	<u>PSV (%)</u>
	Phenylethyl formate	0
	CP formate (cyclohexane-1-methanol-	
55	alpha-3,3-trimethyl formate from IFF)	0

5	xiv) Saturated aliphatic ketones:	<u>PSV (%)</u>
	Fleuramone (2n-heptylcyclopentanone from IFF)	0
10	Orivone (4-(1,1-dimethylpropyl)- cyclohexanone from IFF)	0
15	xv) Unsaturated alcohols:	<u>PSV (%)</u>
	<u>Primary</u>	
	9-Decenol-1	6
	Cinnamic alcohol	0
20	Geraniol	0
	Citronellol	0
	<u>Secondary</u>	
25	Amylvinyl carbinol	0
	<u>Tertiary</u>	
	alpha-Terpineol	0
30	Linalol	0
35	xvi) Unsaturated esters:	<u>PSV (%)</u>
	Florocyclene (hexahydro-4, 7-methanoinden-5-yl propionate from Quest International)	0
	Linalyl acetate	0
40	Terpinyl acetate	0
	Jasmacyclene (hexahydro-4, 7-methanoinden-5-yl acetate from Quest International)	4
45	xvii) Unsaturated ketones:	<u>PSV (%)</u>
	alpha-iso-Methylionone	0
50	Lixetone (acetylated cedarwood from Quest International)	0
55	alpha-Ionone	0

xviii)	Unsaturated nitriles:	<u>PSV (%)</u>
5	Geranyl nitrile	0
	Palmanitrile (isomeric mixture of bicyclic nitriles from Dragoco)	1
10	xix) Unsaturated esters:	<u>PSV (%)</u>
	Pelargene (from Quest International)	0
15	xx) Unsaturated phenols:	<u>PSV (%)</u>
	Eugenol	12
20	xxi) Unsaturated aldehydes:	<u>PSV (%)</u>
	Hexylcinnamic aldehyde	5
	Amylcinnamic aldehyde	0
25	Triplal (mixture of 3,5-dimethyl-3-cyclohexene-1-carboxaldehyde and 2,4-dimethyl-3-cyclohexene-1-carboxaldehyde from IFF)	0
30	xxii) Unsaturated epoxides:	<u>PSV (%)</u>
	Myroxide (cis/trans isomers of ocimene epoxide from Firmenich of Geneva, Switzerland)	0

Examples of perfume compositions satisfying the requirements of the present invention are given below.

40 Composition A

<u>Component</u>	<u>Class</u>	<u>Parts per thousand</u>
45 decanol	(i)	50
phenylpropyl alcohol	(i)	60
50 diphenylmethane	(ix)	50
Herboxane	(vii)	100

55

	dimethylbenzylcarbiny l acetate(ii)	150	
5	p-tertbutylcyclohexyl acetate		
	(ii)	175	
	dihydroterpineol	(i)	30
	tetrahydrolinalol	(i)	150
10	Cedramber	(vi)	40
	hexadecanolide	(iv)	50
	Anther	(vi)	35
15	phenylethyl alcohol	(i)	60
	Traseolide	(iii)	50

20			1,000

Composition B

	Component	Class	Parts per thousand
30	dodecyl nitrile	(v)	5
	diphenylmethane	(ix)	10
	carvacrol	(viii)	5
	Herboxane	(vii)	75
	phenylethyl alcohol	(i)	350
35	dimethylbenzylcarbiny l acetate	(ii)	80
	phenylpropyl alcohol	(i)	50
	Celestolide	(vi)	20
	Traseolide	(iii)	175
40	Moskene	(x)	30
	decanol	(i)	40
	Anther	(vi)	60
	tetrahydrolinalyl acetate	(ii)	50
45	p-tertbutylcyclohexyl acetate	(ii)	50
			1,000

Composition C

50	Component	Class	Parts per thousand
	phenylethyl alcohol	(i)	300
	decanol	(i)	10
55	tetrahydrolinalol	(i)	50
	tetrahydrogeraniol	(i)	3
	p-tertbutylcyclohexyl acetate	(ii)	150

Continuation of the Table on the next page

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(continued)

Component	Class	Parts per thousand
Traseolide	(iii)	200
hexadecanolide	(iv)	10
Cedramber	(vi)	10
Moskene	(x)	30
Herboxane	(vii)	62
Frescile	(v)	5
dihydroterpineol	(i)	20
phenylpropyl alcohol	(i)	150
		<u>1,000</u>

Composition D

<u>Component</u>	<u>Class</u>	<u>Parts per thousand</u>
phenylethyl alcohol	(i)	250
phenylpropyl alcohol	(i)	100
o-tert.butylcyclohexyl		
acetate	(ii)	30
dimethylbenzylcarbiny		
acetate	(ii)	180
benzophenone	(iii)	10
Tonalid	(iii)	60
Galaxolide	(vi)	160
Celestolide	(vi)	10
Anther	(vi)	50
Frutonile	(v)	5
methyl naphthyl ketone	(iii)	20
phenylethyl methyl ether	(vi)	35
tetrahydrolinalol	(i)	90

		1,000

Bleach and Detergent compositions:

Detergent compositions containing peracids would be applied mainly to the cleaning of fabrics but are also usable to clean other substrates, e.g. hard surfaces.

Builder and detergent active components are well characterised in the field of detergent technology. Examples of these components are listed hereafter and full descriptions of these and other examples of these components will be found in "Surface Active Agents" by Schwartz and Perry published by Interscience (1949) and Volume II by Schwartz, Perry and Berch published by Interscience (1958). Examples of detergent actives usable at a level of from 5-50% by

weight in the compositions, which may be built or unbuilt, of the invention are present in the general classes of anionic, nonionic amphoteric, betaine and cationic actives. Specific classes usable singly or in admixture are:

- a) alkylaryl sulphonates having an alkyl chain from C10 to C15.
- b) alkyl (C12 to C18) sulphonates, wherein the alkyl group is branched or linear;
- c) alkali metal salts of alkane sulphonates having an alkyl chain length of from C11 to C14, these actives can be prepared by the reaction of a bisulphite ion species with an olefin;
- d) alkene sulphonates having a chain length from C14 to C24;
- e) sulphates of alcohols having chain lengths from 12 to 15, including branched chain alcohols obtainable under the Trade Mark "Dobanol";
- f) alkali metal salts of C8 to C22 long chain fatty acids; and
- g) dialkali metal salts of sulphonated saturated fatty acids having a chain length from C12 to C20;
- h) fatty acid ester sulphonates having from 8 to 20 carbon atoms in the fatty acid chain;
- i) nonionic detergent actives, for example polyoxyalkylene derivatives of alcohols, alkylamides and alkanolamides, polyoxyalkylene esters of acids, alkylene oxide block polymers (eg. PLURONIC), polyol esters, acyl alkanolamides and ethoxylated alcohols (C8 to C20) having a degree of ethoxylation between 2 and 20. PLURONIC is a trade-mark.

The builder may consist of sequestrant, precipitant or ion-exchange materials, or their mixtures. Specific examples are sodium tripolyphosphate or pyrophosphate, sodium nitrilotriacetate, sodium oxydiacetate, sodium citrate, sodium tartrate and sodium carboxymethyloxy succinate, polymeric carboxylic acid salts derived from one or more of acrylic acid, methacrylic acid, maleic anhydride, and glyoxylic acid, e.g. Builder U of Monsanto, sodium carbonate with or without an insoluble seed material such as calcium carbonate, e.g. calcite, sodium orthophosphate, sodium C16-22 alkyl or alkenyl succinates, sodium C14 to C22 soaps, sodium alpha-sulpho fatty acid salts, soluble silicates and partially soluble layered silicates, amorphous or crystalline alumino-silicates, e.g. zeolites X, Y and A, and mixtures of any of the above. These materials are normally present in an amount of 5 to 80%, preferably from 10 to 60% by weight.

For many applications, a foam controller is desirably present. Non-limiting examples of these are C20 to C24 fatty acids or their salts, alkylphosphates, ethylene distearamide, and hydrophobed mineral particles such as silanised silica, all optionally mixed with hydrocarbon oils, waxes or polydimethylsiloxanes. These may be incorporated in any suitable amount and manner known to the art, e.g. sprayed on to a finished powder either directly or as a dispersion in a liquid carrier, e.g. an ethoxylated alcohol, or sprayed on to a solid porous substrate to form an adjunct which is then added to the formulation.

Stabilising agents for the peracid may also be present. The amount of such agents, when present, is normally small, e.g. from 0.05-10% by weight, preferably from 0.1-5% by weight. Non-limiting examples of these are ethylene diamine tetra-acetic acid, diethylene triamine penta-acetic acid, ethylene diamine tetra-(methylene phosphonic acid), diethylene triamine penta-(methylene phosphonic acid) and their alkali(ne earth) metal salts, dipicolinic acid or its salts, and magnesium silicate.

Other bleaches may be present in addition to the peracid bleach, such as hydrogen peroxide sources e.g. sodium perborate monohydrate and tetrahydrate, optionally with a precursor such as TAED. A list of possible precursors is given in EP-A-0070079 (Unilever).

The composition may include one or more optical brightening agents, such as the diaminostilbene/cyanuric chloride types, e.g. Blankophor MBBH, distyrylbenzene types, e.g. Tinopal CBS and Tinopal BLS, or triazole types, e.g. Blankophor BHC and Tinopal RBS. A combination of Blankophor BHC and Tinopal BLS is preferred for cotton fabrics and Tinopal RBS is preferred for nylon.

Blankophor (ex Bayer) and Tinopal (ex Ciba-Geigy) are trade-marks.

Various polymeric materials are of value as powder structurants, antiredeposition and anti-soiling agents, and for fabric care. Examples of these are the polymers and copolymers of monomers such as acrylic acid, methacrylic acid, and maleic anhydride, polymers and copolymers of ethylene oxide and/or propylene oxide, cellulose ethers, sodium carboxymethylcellulose, and polyvinylpyrrolidone.

Buffering or pH adjusting agents may also be present to achieve a desired acidity or alkalinity. These are normally inorganic salts and examples are sodium metaborate, borax, sodium carbonate or bicarbonate, trisodium orthophos-

phate, disodium hydrogen phosphate, monosodium dihydrogen phosphate, tetrasodium pyrophosphate, trisodium hydrogen pyrophosphate, disodium dihydrogen pyrophosphate, sodium bisulphate, alkaline sodium silicate and neutral sodium silicate. Suitable organic salts and acids may also be used, in addition to or alternative to the inorganic salts. It is desirable that solid buffering agents be used in solid formulations, e.g. powders, but liquid pH adjusting agents, e.g. sulphuric acid, are used in liquid, gel or semi-solid formulations.

A preferred optional ingredient is an enzyme or a mixture of enzymes, which may be proteases and/or lipases. Specific examples of proteases are Alcalase®, Savinase® and Esperase® (obtainable from Novo of Denmark), Maxatase® and Maxacal® (obtainable from Gist-Brocades of Netherlands), Kazusase® (obtainable from Showa-Denko of Japan), Optimase® (obtainable from Miles Kali-Chemie of Hanover, West Germany), and Superase® (obtainable from Pfizer of USA). Specific examples of lipases are fungal lipases obtained from Humicola Lanuginosa or Thermomyces Lanuginosa, and bacterial lipases which react positively with the antibody of the lipase from Chromobacter Viscozum.

The composition may also include materials which confer a soft feel to washed fabrics. These may be one or more of hereinafter described clays at formulation levels of 2-15%, organo-clays at levels of 1-10%, amines and/or cationics at levels of 1.5-10%, silicones at levels of 0.5-5% and cellulase at levels of 0.1-10%.

Suitable clays are phyllosilicate clays with a 2:1 layer structure, the silicate layer being either dioctahedrally or trioctahedrally co-ordinated, and include the species saponite, hectorite, beidellite, or montmorillonite. Such materials are classed as smectite minerals, the most commonly distributed form being the bentonite earths, the major component of which is montmorillonite.

Suitable organo-clays are as described above, with the proviso that the alkali(ne earth) metals or proton exchangeable cations are partially or totally replaced with organic cationic materials.

Suitable amines are primary, secondary, or tertiary mono- or di- C10-C26 alk(en)yl amines; the tertiary dialkylamines in which the third alkyl chain is a C1-C4 alkyl are preferred. Other suitable amines are described in EP-A-0023367 (Procter & Gamble) and are tertiary amines with two C10-C26 alk(en)yl chains with the third group a moiety of several possible structures.

Suitable cationics are water-soluble or insoluble quaternary ammonium compounds of general formula (R1R2R3R4N)+ Y- wherein at least one but not more than two of R1 to R4 is an organic radical containing a group selected from C16-C22 alkyl, or alkylphenyl or alkylbenzyl having to 16 carbon atoms in the alkyl chain, the remaining R groups being selected from hydrocarbonyl groups having 1 to 4 carbon atoms, C2-C4 hydroxyalkyl groups, cyclic structures in which the nitrogen forms part of the ring, e.g. imidazolium compounds, and wherein Y- is a compatible counterion giving electrical neutrality.

Suitable silicones are organofunctional polyalkyl siloxanes, e.g. as described in EP-A-0150867 (Procter & Gamble).

Suitable cellulases are bacterial or fungal cellulases having a pH optimum between 5 and 11.5, e.g. as described in GB-A-2075028 (Novo), GB-A-2095275 (Kao Soap), or GB-A-2094826 (Kao Soap).

Cellulose ethers at a formulation level of 0.05-5% may be used as a deposition aid with 2-40% of an organic hydrophobic softening material such as a calcium soaps, amines, cationics and mixtures of these. Suitable cellulose ethers are nonionic substituted cellulose ethers with an HLB between 3.1 and 3.8, gel points of less than 58°C and contain substantially no hydroxyalkyl groups containing more than two carbon atoms.

Other ingredients, for example starch, colouring materials, corrosion inhibitors, opacifiers, germicides and fillers, e.g. sodium sulphate, talc, calcite are optionally present.

The detergent formulation may be granular, liquid, a solid bar, or a semi-solid, e.g. a gel or paste. It may be supplied in bulk, e.g. in a packet or bottle, or in unit dose form, e.g. sachets or tablets.

Gelled formulations containing the peracid as a solid suspension may require a thickening agent. Suitable thickening agents may be organic or inorganic, and examples are Laponite® or smectite clays, colloidal silicas, natural starches, gums and mucilages, e.g. corn, rice, and wheat starches, gum agar, gum arabic, and carrageenan, modified natural polymers, e.g. starch esters, carboxymethyl cellulose, cellulose ethers, and hydrolysed proteins and synthetic polymers, e.g. polyacrylamides, polymers and copolymers of acrylic acid, methacrylic acid and maleic anhydride monomers. The level of thickener used depends on the level and type of salts present in the formulation, but the gel will normally have a viscosity of 200-100,000 centipoise, preferably 200-20,000 centipoise.

EXAMPLES OF POWDER FORMULATIONS

% in formulation

COMPONENT

	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>VI</u>
Linear Alkylbenzene Sulphonate	6	9	4	9	6	9
Nonionic 7 EO	7	4	9	4	7	4
STPP	23	33	-	-	10	-
Zeolite 4A	-	-	25	20	20	40
NTA	-	-	-	5	-	-
Sodium carbonate	-	-	5	-	-	-
Polyacrylic acid	2	-	-	2	-	1.5
Acrylate/maleate copolymer	-	-	5	-	-	-
Alkaline Silicate	7	6	-	-	3	-
Neutral Silicate	-	-	-	-	-	-
DPDDA granules	20	20	20	4	-	-
(12% active content)				20	20	20

(CONT.)

<u>COMPONENT</u>	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>VI</u>
Sodium bicarbonate	10	10	4	-	10	-
Sodium sulphate	12	4	14	21	10	11
SCMC	1	1	1	1	1	1
EDTA	0.2	0.2	0.2	0.2	0.2	0.2
Perfume Composition A	-	-	0.3	-	-	-
Perfume Composition B	0.3	-	-	0.3	-	-
Perfume Composition C	-	0.3	-	-	-	0.3
Perfume Composition D	-	-	-	-	0.3	-
Water, Minors	-----	-----	----	up to 100	-----	-----

The minor components include for example additional stabilisers, fluoescers, enzymes and foam control systems.

EXAMPLE OF LIQUID FORMULATION

Component	% in formulation VII
Linear alkylbenzene sulphonate	7
Nonionic 7EO	3
Sodium sulphate	7
EDTA	0.5
DPDDA (100% active ingredient)	10
Perfume Composition A	0.2
Water, minors	to 100

One minor component is a pH adjusting agent to bring the pH into the range 2.5 to 6.5, more preferably 3.5 to 4.5.

EXAMPLES OF GEL FORMULATIONS

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<u>Component</u>	<u>% in formulation</u>		
	<u>VIII</u>	<u>IX</u>	<u>X</u>
DPDDA (100% active ingredient)	15	10	15
Laponite [®]	-	-	6
Polyacrylic acid*	-	1	-
Corn starch	13	-	-
Perfume Composition B	0.3	-	-
Perfume Composition C	-	0.25	-
Perfume Composition D	-	-	0.25
Citric acid	0.3	-	0.3
KH ₂ PO ₄	-	1	-
EDTA	0.2	0.2	0.5
Water	-----	to 100	-----

* M.W. ca 4×10^6 .

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Claims

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1. A bleach composition comprising an organic peracid bleach and a perfume composition comprising perfume components which do not contain alkenyl or alkynyl groups and have a PSV (Peracid Stability Value) of at least 65%, selected from the following classes:

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- i) saturated alcohols
- ii) saturated esters
- iii) saturated aromatic ketones
- iv) saturated lactones

- v) saturated nitriles
- vi) saturated ethers
- vii) saturated acetals
- viii) saturated phenols
- ix) saturated hydrocarbons and
- x) saturated aromatic nitromusks

the said perfume components constituting from 0.05 to 1% by weight of the bleach composition.

2. A bleach composition according to claim 1, characterised in that it comprises an effective amount of said organic peracid bleach and up to 10% by weight of said perfume composition.
3. A bleach composition according to claim 1 or claim 2, characterised in that said perfume composition comprises at least 80% by weight of said defined perfume components.
4. A bleach composition according to any one of claims 1 to 3, characterised in that said perfume components have a PSV of at least 80%.
5. A bleach composition according to any one of claims 1 to 4, characterised in that it further contains a detergent active material.
6. A bleach composition according to any one of claims 1 to 5, characterised in that the said organic peracid bleach is 1,12-diperoxy-dodecanedioic acid.
7. A bleach composition according to any one of claims 1 to 6, wherein perfume components constituting from 0.05 to 1% by weight of the bleach composition are selected from:
 - i) Saturated alcohols: Tetrahydrogeraniol Decanol Phenylethyl alcohol Phenylpropyl alcohol o-tert-Butylcyclohexanol Dihydroterpineol di-Isobutylcarbinol 2,6-Dimethyl-2-heptanol Tetrahydrolinalol
 - ii) Saturated esters: Tetrahydrolinalyl acetate Methyl acetate ortho-tert-Butylcyclohexyl acetate Dimethyl benzyl carbinyl acetate
 - iii) Saturated aromatic ketones: 6-Acetyl-1,1,3,4,4,6-hexamethyltetrahydronaphthalene Benzophenone Methyl naphthyl ketone 6-Acetyl-1-isopropyl-2,3,3,5-tetramethylindane 4-Acetyl-6-tertbutyl-1,1-dimethyl indane
 - iv) Saturated lactones: Hexadecanolide Sclareolide gamma-Lactone of 1-hydroxy-3,10,10-trimethyl-bicyclo [4,4,10] decane-3-carboxylic acid
 - v.) Saturated nitriles: 2-Methyldecanonitrile Dodecyl nitrite 3-Methyldodecanonitrile
 - vi) Saturated ethers: Cedryl methyl ether Iso-amyl phenylethyl ether Phenylethyl methyl ether
 - vii) Saturated acetals: 2-Butyl-4,4,6-trimethyl dioxan Indano [1,2-d]1,3-dioxane
 - viii) Saturated phenols: Carvacrol
 - ix) Saturated hydrocarbons: Diphenyl methane para-Cymene
 - x) Saturated aromatic nitromusks: Musk cymene

Patentansprüche

1. Bleichmittelzusammensetzung, umfassend ein organisches Persäurebleichmittel und eine Parfümkomposition, umfassend Parfümbestandteile, die keine Alkenyl- oder Alkynylgruppen enthalten und einen PSV-Wert (Persäurestabilitätswert) von mindestens 65 % aufweisen, ausgewählt aus den folgenden Klassen:

- i) gesättigten Alkoholen
- ii) gesättigten Estern
- iii) gesättigten aromatischen Ketonen
- iv) gesättigten Lactonen
- v) gesättigten Nitrilen
- vi) gesättigten Ethern
- vii) gesättigten Acetalen
- viii) gesättigten Phenolen
- ix) gesättigten Kohlenwasserstoffen und
- x) gesättigtem aromatischem Nitromoschus,

wobei die Parfümbestandteile 0,05 bis 1 Gew.-% der Bleichmittelzusammensetzung ausmachen.

2. Bleichmittelzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie eine wirksame Menge des organischen Persäurebleichmittels und bis zu 10 Gew.-% der Parfümkomposition umfaßt.
3. Bleichmittelzusammensetzung nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß die Parfümkomposition mindestens 80 Gew.-% der definierten Parfümbestandteile umfaßt.
4. Bleichmittelzusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Parfümkomponenten einen PSV-Wert von mindestens 80 % aufweisen.
5. Bleichmittelzusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß sie außerdem einen Waschmittelaktivstoff enthält.
6. Bleichmittelzusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das organische Persäurebleichmittel 1,12-Diperoxydodecandisäure ist.
7. Bleichmittelzusammensetzung nach einem der Ansprüche 1 bis 6, worin die Parfümbestandteile, 0,05 bis 1 Gew.-% der Bleichmittelzusammensetzung ausmachen, ausgewählt aus:
 - i) Gesättigten Alkoholen: Tetrahydrogeraniol Decanol Phenylethylalkohol Phenylpropylalkohol o-tert.-Butylcyclohexanol Dihydroterpineol Diisobutylcarbinol 2,6-Dimethyl-2-heptanol Tetrahydrolinalol
 - ii) Gesättigten Estern: Essigsäuretetrahydrolinalylester Essigsäuremethylester Essigsäure-ortho-tert.-butylcyclohexylester Essigsäuredimethylbenzylcarbinyylester
 - iii) Gesättigten aromatischen Ketonen: 6-Acetyl-1,1,3,4,4,6-hexamethyltetrahydronaphthalin Benzophenon Methylnaphthylketon 6-Acetyl-1-isopropyl-2,3,3,5-tetramethylindan 4-Acetyl-6-tert.-butyl-1,1-dimethylindan
 - iv) Gesättigten Lactonen: Hexadecanolid Sclareolid γ -Lacton von 1-Hydroxy-3,10,10-trimethylbicyclo-[4,4,10]decan-3-carbonsäure
 - v) Gesättigten Nitrilen: 2-Methyldecannitril Dodecylnitril 3-Methyldodecannitril
 - vi) Gesättigten Ethern: Cedrylmethylether Isoamylphenylether Phenylmethylether
 - vii) Gesättigten Acetalen: 2-Butyl-4,4,6-trimethyldioxan Indano[1,2-d]1,3-dioxan
 - viii) Gesättigten Phenolen: Carvacrol
 - ix) Gesättigten Kohlenwasserstoffen: Diphenylmethan p-Cymen
 - x) Gesättigtem aromatischem Nitromoschus: Moschuscymen

Revendications

1. Une composition de blanchiment comprenant un agent de blanchiment peracide organique et une composition de parfum comprenant des composants de parfum qui ne contiennent pas de groupes alkényle ni alkynyle et présentent une PSV (valeur de stabilité au peracide) au moins égale à 65 %, sélectionnés parmi les classes suivantes :

- i) alcools saturés
- ii) esters saturés
- iii) cétones aromatiques saturées
- iv) lactones saturées
- v) nitriles saturés
- vi) éthers saturés
- vii) acétals saturés
- viii) phénols saturés
- ix) hydrocarbures saturés et
- x) nitromuscs aromatiques saturés

lesdits composants de parfum constituant 0,05 à 1% en masse de la composition de blanchiment.

2. Une composition de blanchiment selon la Revendication 1, caractérisée en ce qu'elle comprend une quantité efficace dudit agent de blanchiment peracide organique et jusqu'à 10 % en masse de ladite composition de parfum
3. Une composition selon la Revendication 1 ou la Revendication 2, caractérisée en ce que ladite composition de parfum comprend au moins 80 % en masse desdits composants de parfum définis.
4. Une composition de blanchiment selon l'une quelconque des Revendications 1 à 3, caractérisée en ce que lesdits composants de parfum présentent une PSV au moins égale à 80 %.
5. Une composition de blanchiment selon l'une quelconque des Revendications 1 à 4, caractérisée en ce qu'elle comprend en outre une matière détergente active.
6. Une composition de blanchiment selon l'une quelconque des Revendications 1 à 5, caractérisée en ce que ledit agent de blanchiment peracide organique est de l'acide 1,12-diperoxydodécane dioïque.
7. Une composition de blanchiment selon l'une quelconque des Revendications 1 à 6, dans laquelle les composants de parfum constituant 0,05 à 1 % en masse de la composition de blanchiment sont sélectionnés parmi :

i) Alcools saturés : Tétrahydrogéraniol Décanol Alcool de phényléthyle Alcool de phénylpropyle O-tert-butylcyclohexanol Dihydroterpinéol Di-isobutylcarbinol 2,6-diméthyl-2-heptanol Tétrahydrolinalol

ii) Esters saturés : Acétate de tétrahydrolinalyle Acétate de méthyle Acétate d'ortho-tert-butylcyclohexyle Acétate de diméthylbenzylcarbinyle

iii) Cétones aromatiques saturées : 6-acétyl-1,1,3,4,4,6-hexaméthyltétrahydronaphtalène Benzophénone Méthylnaphtylcétone 6-acétyl-1-isopropyl-2,3,3,5-tétraméthylindane 4-acétyl-6-tertbutyl-1,1-diméthylindane

iv) Lactones saturées : Hexadécanolide Sclaréolide Gammalactone d'acide 1-hydroxy-3,10,10-triméthyl-bicyclo [4,4,10]décane-3-carboxylique

v) Nitriles saturés : 2-méthyl-décanonitrile Nitrile de dodécyle 3-méthyl-dodécanonitrile

vi) Ethers saturés : Cédrylméthyléther Iso-amylphényléthyléther Phényléthylméthyléther

vii) Acétals saturés : 2-butyl-4,4,6-triméthyl-dioxane Indano[1,2-d]1,3-dioxane

viii) Phénols saturé : Carvacrol

ix) Hydrocarbures saturés : Diphénylméthane Para-cymène

x) Nitromuscs aromatiques saturés : Cymène de musc

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